

09/701681

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

INTERNATIONAL APPLICATION NO.

PCT/FR99/01279

INTERNATIONAL FILING DATE

1 JUNE 1999

PRIORITY DATE CLAIMED

3 JUNE 1998

TITLE OF INVENTION

POLYACRYLATES WITH IMPROVED BIODEGRADABILITY

APPLICANT(S) FOR DO/EO/US

Christian GANCET et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith.
 - b. ☐ has been transmitted by the International Bureau (see accompanying PCT Form 308).
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 - ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 - ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
 - ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 - ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
- ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 - ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
 - ☐ A SECOND or SUBSEQUENT preliminary amendment.
 14. ☐ A substitute specification.
 15. ☐ A change of power of attorney and/or address letter.
 16. ☒ Other items or information:
 - a. PCT/RO/101 (in French);
 - b. PCT/IPEA/416 and PCT/IPEA/409 (both in French);
 - c. International Search Report PCT/ISA/210 (attached to IDS) (in English and in French); and
 - d. PCT Publication No. WO 99/62971.

(Page 2)

U. S. DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

33808F138 (1798-7368)

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (if known,
see 37 CFR 1.5)

09/701681

17. ☒ The following fees are submitted:

CALCULATIONS

PTO USE ONLY

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search Report has been prepared by the EPO or JPO \$860.00

International preliminary examination fee paid to USPTO

(37 CFR 1.482) \$690.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international
search fee paid to USPTO (37 CFR 1.445(a)(2)) \$710.00Neither international preliminary examination fee (37 CFR 1.482) nor
international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1,000.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(2)-(4) \$100.00**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from
earliest claimed priority date (37 CFR 1.495(e)).

\$---

Claims	Number Filed	Number Extra	Rate		
al Claims	-20 =	---	x \$18.00	---	
pendent Claims	-3 =	---	x \$78.00	---	
multiple dependent claim(s) (if applicable)			+ \$270.00	---	

TOTAL OF ABOVE CALCULATIONS =

\$ 860.00

Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must
be filed. (Note 37 CFR 1.9, 1.27, 1.28).

SUBTOTAL =

\$ 860.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months
from the earliest claimed priority date (37 CFR 1.492(f)).

+

TOTAL NATIONAL FEE =

860.00

for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property.

+

TOTAL FEES ENCLOSED =

860.00

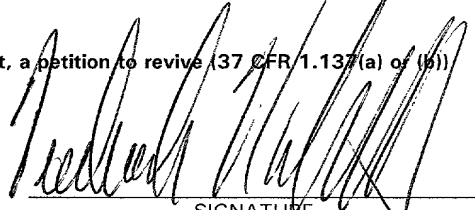
Amount to be
refunded \$

charged \$

a. ☒ A check in the amount of \$ 860.00 to cover the above fees is enclosed.b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to
Deposit Account No. 02-4300.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b))
must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

SMITH, GAMBRELL & RUSSELL, LLP
The Beveridge, DeGrandi, Weillacher & Young
Intellectual Property Group
1850 M Street, N.W., Suite 800,
Washington, D.C. 20036
Telephone: (202) 659-2811
Facsimile: (202) 659-1462



SIGNATURE

Frederick F. Calvetti
NAME

28,557

REGISTRATION NO.

Date: December 1, 2000

09/701681

PCT Rec'd

1 JUN 2001

POLYACRYLATES WITH IMPROVED BIODEGRADABILITY

The invention relates to biodegradable polymers and in particular to polyacrylates with improved biodegradability.

The polyacrylates of the invention can be used in various applications and in particular in detergent compositions.

In general, detergent compositions involve a certain number of chemical products. These should be biodegradable so as not to harm the environment. Detergent compositions and cleaning agents conventionally contain phosphates. These are highly effective and relatively non-toxic, but cause eutrophization of natural aquatic media.

Phosphates have been partially replaced in detergent formulations by polymers such as polyacrylic acids or copolymers based on acrylic acid and on maleic anhydride.

Although the polyacrylates currently used do not pose this problem, their absence of rapid biodegradability causes an accumulation in the natural environment (Swift, Polymer Degradation and Stability, 45, 215-231, 1994).

No toxicity associated a priori with these polymers is known, but their long-term effect is uncertain, and this uncertainty has contributed towards the instigation of numerous research studies intended to improve their biodegradability.

It is clearly established that hydrophilic polymers, such as polyvinyl alcohol, are rapidly degraded by microorganisms (Macromol. Chem. Phys. 196, 3437, 1995). It is also known that polyacrylic acids with an average molecular weight of less than 1000 have better biodegradability than their higher homologs (Swift, Ecological Assessment of Polymer 15, 291-306, 1997).

EP 0 497 611 discloses the preparation of biodegradable terpolymers and of compositions containing them. These terpolymers are based on vinyl acetate, acrylic acid and maleic anhydride. They have
5 weight-average molecular masses of less than 20 000.

US 5 318 719 discloses a novel class of biodegradable materials based on the grafting of polymers containing acidic functions onto a polyoxyalkylene-based biodegradable support.

10 Other studies indicate that chains comprising hetero atoms are more readily degraded than carbon-based chains. Thus, US 4 923 941 discloses biodegradable copolymers containing carboxylic acid functions and heterocycles, as well as the detergent
15 compositions containing them.

The Applicant has now found that the degradability of the polymers described above can be improved by inserting sites of fragility into the main chain. These sites will be rapidly broken by the
20 microorganisms of the natural environment, to give acrylic blocks that are small enough in mass to be readily biodegradable.

The Applicant has found that the insertion of electron-rich centres, such as double bonds, into an
25 acrylic chain makes the acrylic chain more fragile with respect to microorganisms and thus improves its biodegradability.

It is moreover well known that although carbon-based chains are highly chemically and biologically
30 resistant, this is true only in the case of saturated chains. The reason for this is that if a chain comprises multiple bonds (electron-rich), these readily oxidizable and chemically reactive bonds will constitute the first sites of cleavage of the molecule.
35 Among the multiple bonds, carbon-carbon double bonds appear to be the ones most readily usable.

The invention relates to hydrophilic polymers with improved biodegradability, in particular

polyacrylates containing readily oxidizable electron-rich sites.

The polymers of the invention contain:

- from 70% to 99% by weight of units derived by polymerization from at least one monomer A bearing a carboxylic acid function or an equivalent function,
- from 1% to 30% by weight of units derived by polymerization from at least one monomer B bearing an electron-rich group or a function capable of introducing an electron-rich group into the main chain,
- from 0% to 29% by weight of units derived by polymerization from at least one monomer C which is copolymerizable with A and B, but is different from A and B.

They can also contain a chain-limiting transfer agent.

Irrespective of the monomers A, B and C, the final polymer should remain hydrophilic.

The monomer A is chosen from the group consisting of monomers bearing at least one carboxylic acid and derivatives thereof, such as acid salts and anhydrides. As a non-limiting guide, mention may be made of maleic anhydride, acrylic acid, methacrylic acid, itaconic acid, fumaric acid and maleic acid, and the salts thereof.

The monomer A which is preferred according to the invention is acrylic acid.

The monomer B is chosen from the group consisting of:

monomers bearing two conjugated double bonds, such as butadiene, isoprene, chloroprene, dimethylbutadiene, cyclohexadiene, butadienecarboxylic acid and butadienedicarboxylic acid, and

monomers bearing a triple bond, such as acetylene, acetylenecarboxylic acid and acetylenedicarboxylic acid.

The preferred monomer B of the invention is isoprene.

The monomer C, which is different from A and B, is chosen from the group containing monomers that are copolymerizable with A and B, such as vinyl, acrylic and styrene monomers, and derivatives thereof.

5 The distribution in the final polymer of the fragile sites provided by the monomer B depends both on the intrinsic relative reactivity of the various monomers present and on the ratio of the relative concentrations of monomer A, monomer B and optionally
10 other monomers C.

The polymers of the invention may be linear or branched. They may also be partially crosslinked.

Polyacrylic acids partially neutralized and crosslinked with the aid of a molecule containing at
15 least two functions that are reactive with carboxylic acids and containing the fragile sites described above constitute a perfect example of branched polymers with improved biodegradability according to the invention.

Among these polymers, mention may be made of
20 the products generally used as aqueous-liquid absorbing agents and often referred to as superabsorbents (SAPs).

The polymers of the invention may be obtained by the joint polymerization of:

70% to 99% by weight of at least one monomer A,
25 1 to 30% by weight of at least one monomer B,
and

0% to 29% by weight of at least one monomer C.

The monomers A, B and C are those described above.

30 The polymerization may be carried out in solution in an organic solvent or in the presence of water. As a guide, these two modes of synthesis are described for the production of a linear product:

- in the presence of organic solvent:

35 The polymerization takes place in tetrahydrofuran (THF). When the polymerization is performed batchwise, the monomer mixture is introduced into the solvent along with the initiator (azobis-isobutyronitrile, AIBN) and, where appropriate, a

transfer agent such as thioglycolic acid (TGA) or another thiol.

After degassing and placing under nitrogen, the reaction is initiated by raising the temperature to 70°C.

The monomers A, B and C, if used, may be introduced continuously with the aid of a metering pump into the reactor throughout the reaction, with the aim of better distributing the functional monomer throughout the chain and of thus obtaining a polymer of more uniform composition.

After reaction and concentration of the THF on a rotary evaporator, the polymer is precipitated and dried in an oven under vacuum.

- in the presence of water:

The monomer mixture, the initiator (potassium persulphate, $K_2S_2O_8$) and, where appropriate, a transfer agent such as thioglycolic acid (TGA) or another thiol, are introduced into the water.

After degassing and placing under nitrogen, the reaction is initiated by raising the temperature to 70 or 80°C.

After polymerization, the product is recovered by evaporation and drying under vacuum.

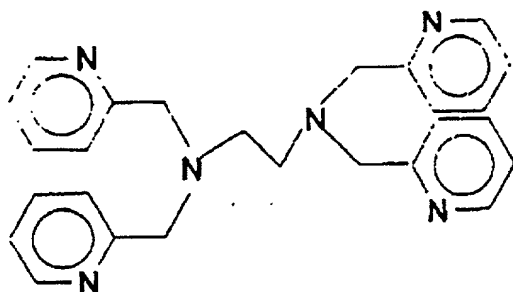
The biodegradability of the products obtained is examined in the following way:

Evaluation of the biodegradability

Oxidative prescreening

This test is intended to evaluate the sensitivity of the new sequences to the action of oxidative degradation of microbial enzymes.

Given that the oxidative enzymes are neither easy to use nor commercially available, the test method described below uses metal complexes, which are analogs of oxidative enzymes, and in particular TPEN N,N,N',N' -tetramethylpyridine-1,2-ethylenediamine or N,N,N',N' -tetrakis(2-pyridylmethyl)ethane-1,2-diamine.



combined with Fe(III)

The reaction conditions used for the degradability test are as follows:

5

Polymers to be tested	: 1 mg/ml (test volume = 10 ml)
TPEN combined with Fe(III)	: 0.05 mM
Free TPEN	: 0.5 mM
H ₂ O ₂	: 100 mM
pH	: 7
Temperature	: 50°C
Time	: 4 h

The evaluation of the level of degradation obtained is made by liquid chromatography under the following conditions:

Column	: Tosohaas TSK 3000
Eluent	: 0.1 M H ₃ CCOONa
Flow rate	: 0.5 ml/min.
Injection	: 25 µl after 0.22 µ filtration
Detection	: Differential refractometer
Data acquisition	: Dionex Peaknet

10 The column is calibrated by means of polyacrylate standards (Polymer Laboratories).

The degradability of the polymer under the test conditions is measured by the shift of the peak observed in liquid chromatography towards lower molecular masses.

15 This shift is quantified by means of a degradability index I₁₀₀₀ defined in the following way:

- Initial mass of the polymer	: Mi
- Final mass of the polymer	: Mr
- Number of cleavages	: Nc

- Initial degree of polymerization : $D_p = \frac{M_i}{M_{mono}}$

- with M_{mono} : "average" mass of the monomer

- degradability index: $I_{1000} = \frac{N_c}{D_p} \times 1000$

i.e.: $I_{1000} = \left(\frac{M_i}{M_r} - 1 \right) \times \frac{M_{mono}}{M_i} \times 1000$

Microbiological degradation

5 Experimental cultures

Candida tropicalis cultures are prepared on a liquid medium comprising malt extract (20 g.l⁻¹) and incubated at 30°C with axial agitation for 48 hours.

10 These cultures are centrifuged at 18 000 rpm for 15 minutes and the pellet is washed with 0.1 M pH6 phosphate buffer and is recentrifuged as described above. The latter operation is carried out a second time in order to effectively remove any residual substrate.

15 Warburg method

The evaluation of the respiration of *C. tropicalis* on a polyacrylate is carried out in Warburg flasks (total volume of 3 ml) comprising 1.3 ml of 0.1 M pH6 phosphate buffer, 1 ml of yeast suspension
20 (about 3 mg dry weight) and 0.5 ml of polyacrylate at 1.12 g/l⁻¹ (final concentration of 200 ppm).

Control tests are carried out in parallel:

25 - a flask containing only phosphate buffer (2.8 ml) allows the atmospheric pressure variations to be measured

- the endogenous respiration is measured in a flask containing only phosphate buffer (1.8 ml) and the yeast suspension (1 ml)

30 - the respiration due to contaminants which may be present in the acrylate solution is also evaluated by a test comprising the acrylate (0.5 ml) and the phosphate buffer (2.3 ml).

The flasks are agitated in a water bath at 30°C.

Measurements of the pressure variations due to the appearance of CO_2 , which is indicative of the metabolism of the acrylate by the yeast, are carried out every 15 minutes.

5 *Cultures of C. tropicalis on polyacrylate*

Two types of culture are carried out: cultures exclusively comprising polyacrylate as carbon source and cultures combining yeast extract. The first case makes it possible to indicate the use of the compound by the microorganism. The second case is directed towards optimizing this use in order to increase the degradation efficiency by promoting the growth of the yeast.

In both cases, these media comprise a conventional mineral medium ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ g; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 0.1 g; NaCl 1 g; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.1 g; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 0.1 g; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 0.1 g; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 10 mg; $\text{AlK} (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ 10 mg; H_3BO_3 10 mg; $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 2mg; qs 1 l distilled water) combined with 0.1 M pH6 phosphate buffer in proportions of 2/98. The polyacrylate is at a final concentration of 500 ppm.

The yeast extract which may be added has a final concentration of 200 ppm. This concentration may be increased up to 500 ppm if the growth remains too little. The flasks are incubated at 30°C with transverse agitation and are subcultured after one week. The cultures are then continued for 15 days under the same conditions.

Evaluation of the calcium-complexing ability

30 The principle of this test consists in measuring the ability of a given polymer to prevent the formation of a precipitate of CaSO_4 from sodium sulphate and calcium chloride.

The protocol used is as follows:

35 Two aqueous solutions are prepared starting with distilled water, to contain the following salts:

Solution A: $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	64.9 g/l + MgCl_2 0.5 g/l
Solution B: Na_2SO_4	62.7 g/l

400 ml of distilled water are introduced into a 500 ml flask and 50 ml of solution A is gradually added thereto, with agitation, followed by 50 ml of solution B. In a flask serving as control, nothing else is added, while a certain amount of antitartar agent is added to the other two flasks. At time $t = 0$, after homogenization of the solutions, a few ml of solution are taken and the calcium and magnesium therein are assayed. The flasks are stoppered and then left to stand for 7 days. A few ml of supernatant liquid are then taken and the calcium and magnesium are re-assayed.

The ion concentration is measured by emission spectrometry using the ICP (Inductively Coupled Plasma) technique.

The results obtained are expressed as ppm of calcium in the solutions at time 0 and after 7 days of contact.

The examples which follow illustrate the invention without limiting its scope.

Example 1 (comparative)

Acrylic acid (AA)/vinyl monomer copolymer in solvent phase

50 ml of tetrahydrofuran (THF), 5.76 g of acrylic acid, 0.98 g of maleic anhydride, 2 g of ethylene glycol vinyl ether (EGVE) and 0.296 g of azo-bis-isobutyronitrile (AIBN) are introduced into a 100 ml two-necked round-bottomed flask fitted with a condenser and a nitrogen inlet.

The reaction mixture is degassed by a succession of vacuum and nitrogen cycles and is then placed in an oil bath thermostatically maintained at 70°C.

After reaction for 12 hours the reaction mixture is concentrated on a rotary evaporator and then precipitated (twice) filtered (sinter 5) and dried in an oven under vacuum (5×10^{-2} bar) for a minimum of six hours.

Results

Ref.	Composition	T°C	Transfer agent	Initiator	I ₁₀₀₀
BG 78	AABO/AM10/EGVE10	68 (reflux)	No	AIBN	56

Oxidative degradability

Under the test conditions, the product obtained has a degradability index I₁₀₀₀ of 56, this result being higher than that of the reference polyacrylates, whose I₁₀₀₀ is between 18 and 26 under the same conditions.

Similarly, a commercial copolymer of methyl vinyl ether and of maleic anhydride, Gantrez, has an I₁₀₀₀ of 46.5, which clearly confirms the biodegradability of the polycarboxylic-vinyl copolymers.

Finally, a polyvinyl alcohol homopolymer with very good biodegradability has an I₁₀₀₀ of 212.1, which may thus be considered as the upper limit under the test conditions.

Example 2

AA/isoprene copolymer in solvent phase

1. Batchwise synthesis at the reflux point of the solvent (68°C)
20 ml of tetrahydrofuran, 2.88 g of acrylic acid, 0.68 g of isoprene, 0.082 g of AIBN and 0.131 g of thioglycolic acid (TGA) as transfer agent, if necessary, are introduced into a 100 ml Schlenck tube.

The reaction mixture is degassed by a succession of vacuum and nitrogen cycles and is then placed in an oil bath thermostatically maintained at 70°C.

After reaction for 12 hours, the reaction mixture is concentrated on a rotary evaporator and then precipitated (twice), filtered (sinter 5) and dried in an oven under vacuum 5×10^{-2} bar) for a minimum of six hours.

Two products were prepared according to this method. They have the reference numbers BG 70 and BG 115.

2. Semi-continuous synthesis in a reactor under pressure (70°C; 2.5 bar)

0.6 g of AIBN, 33.5 g of acrylic acid and 90 g of THF are introduced into a 500 ml stainless-steel reactor able to withstand a minimum pressure of 5 bar, fitted with a magnetic stirring bar.

The reactor is hermetically closed by a lid with 8 screws, on which is mounted a manometer and a valve which can be used to introduce liquids and to degas the reactor.

The pressure in the reactor is raised to 2.5 bar by introduction of nitrogen.

7.5 g of isoprene and 180 g of THF are weighed into a flask, thermostatically maintained by an ice bath. The filled flask is placed on a balance to monitor the decrease in mass corresponding to the amount introduced into the reactor. The flask is connected to a metering pump, which is itself connected to the reactor. The connecting tubes are purged and the reactor is placed in an oil bath thermostatically maintained at 70°C and stirred magnetically. There is a risk of the pressure increasing slightly: it should not exceed 5 bar. Introduction of the THF/isoprene mixture into the reactor is then commenced. The addition lasts 180 min and the reaction is maintained at 70°C for a further 17 hours.

At the end of the reaction, the reactor is placed in an ice bath in order to reduce the internal pressure, and after 30 minutes it is degassed.

The reaction mixture is concentrated on a rotary evaporator and then precipitated (twice), filtered (sinter 5) and dried in an oven under vacuum (5×10^{-2} bar) for a minimum of six hours.

The product obtained has the reference number CL 56.

Results

Ref.	Composition	T°C	Transfer agent	Initiator	I ₁₀₀₀
BG 70	AA80/Isopr20	68 (reflux)	No	AIBN	48.6
BG115	AA80/Isopr20	68 (reflux)	Yes	AIBN	62.4
CL 56	AA80/Isopr20	70	No	AIBN	50

Oxidative degradability

Under the test conditions, the products obtained have a degradability index I₁₀₀₀ of between 48.6 and 68.4, this result being higher than that of the reference polyacrylates, whose I₁₀₀₀ is between 18 and 26 under the same conditions. This is confirmed in the presence or absence of a transfer agent. These results show that the degradability of this type of copolymer in the oxidation test is of an entirely equivalent level to that of the structures described in Example 1 corresponding to EP 0 4 97 611.

Microbiological degradability

The AA/isoprene copolymer (BG70) was moreover evaluated in microbiological degradation under the conditions described above. Two types of results were obtained.

a - Respiration test

The copolymer was used as carbon substrate for *Candida tropicalis* cultures, compared with readily metabolized control glucose substrate, and with a reference polyacrylate.

The respiration values obtained are as follows:

Reference	Composition	Respiration, μ l O ₂ /h.g of cells
Glucose	-	17.3
BG70	AA80/Isoprene20	5.1
Norasol 4500	AA Homopolymer	0

Compared with a standard polyacrylate which causes no respiration, the copolymer with isoprene has a specific respiration level of close to 30% of that of glucose, which indicates a marked improvement in biodegradability.

b - Assimilation test

The copolymer was used as carbon substrate for *Candida tropicalis* cultures of longer duration, and analyzed by liquid chromatography comparatively, after culturing for 15 days.

5 The analysis of these results shows that about 72.5% of the copolymer was degraded by the microorganism over the 15 days of culture. Washing of the biomass with saline solutions reveals no trace of polymer, which is proof that biodegradation has taken
10 place, rather than adsorption of the polymer thereon.

Complexation

The copolymers obtained are dissolved in 0.1 M sodium hydroxide before analysis, and are then returned to the test pH. The level of calcium measurable after
15 7 days of contact indicates the ability of the polymer evaluated to inhibit its precipitation in the form of CaSO_4 . The table below indicates that the effect persists up to 0.25 ppm of AA/isoprene copolymer under the test conditions, and up to a similar value for the
20 reference polyacrylate, whereas no effect is measured for the control.

Reference	ppm	Content of Ca^{2+} ppm at $t = 0$	Content of Ca^{2+} ppm at $t = 7$ days
	0.05	2260	1590
BG70	0.25	2290	2290
	0.5	2290	2270
	0.1	1860	890
Norasol 4500	0.4	1780	1530
	1	1790	1680
Control		1930	940

These results make it possible to conclude that the novel AA/isoprene polymers show a power with respect to calcium which is equivalent to that of a
25 reference polyacrylate such as Norasol 4500.

CLAIMS

1. A hydrophilic polymer with improved biodegradability, characterized in that it contains:

- 5 - from 70% to 99% by weight of units derived by polymerization from at least one monomer A bearing a carboxylic acid function or an equivalent function,
- from 1% to 30% by weight of units derived by polymerization from at least one monomer B bearing an
- 10 electron-rich group or a function capable of introducing an electron-rich group into the main chain,
- from 0% to 29% by weight of units derived by polymerization from at least one monomer C which is copolymerizable with A and B, but is different from A
- 15 and B.

2. The hydrophilic polymer as claimed in claim 1, characterized in that the monomer A is chosen from the group consisting of monomers bearing at least one carboxylic acid and derivatives thereof, such as maleic

20 anhydride, acrylic acid, methacrylic acid, itaconic acid, fumaric acid and maleic acid, and the salts thereof.

3. The hydrophilic polymer as claimed in claim 2, characterized in that the monomer A is acrylic acid.

25 4. The hydrophilic polymer as claimed in claims 1 to 3, characterized in that the monomer B is chosen from the group consisting of:

 monomers bearing two conjugated double bonds, such as butadiene, isoprene, chloroprene, dimethyl-

30 butadiene, cyclohexadiene, butadienecarboxylic acid and butadienedicarboxylic acid, and

 monomers bearing a triple bond, such as acetylene, acetylenecarboxylic acid and acetylenedicarboxylic acid.

35 5. The hydrophilic polymer as claimed in claim 4, characterized in that the monomer B is isoprene.

6. The hydrophilic polymer as claimed in one of claims 1 to 5, characterized in that the monomer C is

chosen from the group containing monomers that are copolymerizable with A and B, such as vinyl, acrylic and styrene monomers and derivatives thereof, but which are different from A and B.

5 7. A use of a hydrophilic polymer as claimed in one of claims 1 to 6 in detergent compositions.

8. The hydrophilic polymer as claimed in any one of claims 1 to 6, characterized in that it is crosslinked with a difunctional agent to form a
10 carboxylic polymer which can be used as a superabsorbent.

Declaration and Power of Attorney United States Patent Application

UNITED STATES
Patents and Design Patents
Sole & Joint Inventors
Convention & Non-convention
PCT & Non-PCT
This form cannot be amended, altered
or changed after it is signed
(For use only for inventors who
understand the English language.)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

POLYACRYLATES WITH IMPROVED BIODEGRADIBILITY

(check one) ☒ is attached hereto.

☒ was filed as U.S. Application No. _____ on _____ and (if applicable) was amended on _____.

☐ was filed as PCT International Application No. PCT/FR99/01279 on 1 JUNE 1999 and (if applicable) was amended under PCT Article 34 on _____.

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or §365(b) of any foreign and PCT application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America listed in this Declaration. I have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application(s) on which priority is claimed:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)
98/06939	FRANCE	3 JUNE 1998	YES

I claim the benefit under Title 35, United States Code, §120 or §365(c) of any United States application and PCT international application designating the States of America listed in this Declaration and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the application and the national or PCT international filing date of this application:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

My application is acknowledged for the Preliminary Amendment, which is hereby incorporated by reference as part of the original disclosure.

I claim priority benefits under Title 35 United States Code §119(e) of any U.S. provisional application(s) listed below:

U.S. Provisional Application No.	Filing Date

I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Robert Weilacher (20,531), Herbert M. Hanegan (25,682), Frederick F. Calvetti (28,557), J. Rodgers Lunsford, III (29,405), Michael A. Makuch (32,263), Dennis C. Lunsford (32,936), William F. Rauchholz (34,701), Michael C. Carrier (42,391), Eric J. Hanson (44,738), Patrick R. Delaney (45,338), Donna D. King (45,962), M. Lewinski (46,383) and Brandon S. Boss (46,567).

All correspondence to: Smith, Gambrell & Russell, LLP, Beveridge, DeGrandi, Weilacher & Young Intellectual Property Group, 1850 M Street, N.W., (Suite 300), Washington, D.C. 20036. All facsimiles may be sent to (202) 659-1462. Direct all phone calls to (202) 659-2811.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor: Christian GANCET

Citizenship: FRANCE

Residence (city, state, country): F-64140 Lons, FRANCE

Post office address: 4, rue de la Digue, F-64140 Lons, FRANCE

Signature: _____

Date: 23 April 2001

Full name of second joint inventor, if any: Rosangela PIRRI

Citizenship: FRANCE

Residence (city, state, country): F-64121 Montardon, FRANCE

Post office address: Chemin Romse-Passad, F-64121 Montardon, FRANCE

Signature: _____

Date: 23 April 2001

☐ Additional inventors and/or prior applications are listed in attached Supplemental Sheet(s).

SGR/BDWY

Supplemental Sheet to U.S. Declaration and Power of Attorney (SGR/BDWY-1 supp.)

Additional Inventor(s):

Full name of second joint inventor, if any: Bernard BOUTEVIN *FR4* Citizenship: FRANCE
 Residence (city, state, country): F-34090 Montpellier, FRANCE
 Post office address: 2, rue Anselme Mathieu, F-34090 Montpellier, FRANCE

Signature: [Signature] Date: 06/05/2001

Full name of third joint inventor, if any: Cédric LOUBAT *FR4* Citizenship: FRANCE
 Residence (city, state, country): F-34790 Grabels, FRANCE
 Post office address: Terrasse de l'Oliveraie, 1, rue de l'Oliveraie, F-34790 Grabels, FRANCE

Signature: [Signature] Date: 06/05/2001

Full name of fourth joint inventor, if any: Jean, LEPETIT *FR4* Citizenship: FRANCE
 Residence (city, state, country): F-13190 Allauch, FRANCE
 Post office address: Résidence Chappe, Bâtiment 7, F-13190 Allauch, FRANCE

Signature: [Signature] Date: 03.05.2001

Full name of fifth joint inventor, if any: _____ Citizenship: _____
 Residence (city, state, country): _____
 Post office address: _____

Signature: _____ Date: _____

Additional Foreign/PCT Applications:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)

Additional U.S. Applications:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

Additional Provisional U.S. Applications:

U.S. Provisional Application No.	Filing Date